

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TOKYO OHKA KOGYO CO LTD

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(72)Inventor : TANABE MASAHIITO

WAKIYA KAZUMASA

KOBAYASHI MASAICHI

(54) TREATING SOLUTION COMPOSITION AFTER ASHING AND TREATMENT METHOD USING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a treating solution composition after ashing which prevents the corrosion of metal wiring and reliably removes residue such as a degenerated photoresist film and a metal deposition on a substrate subjected to ashing after dry etching under severer conditions in an ultrafine patterning process in 0.2-0.3  $\mu\text{m}$  or below and can effectively prevent corrosion in the removal of the residue and in water rinsing and to provide a treatment method using the composition.

SOLUTION: The salt of hydrofluoric acid and a metal ion-free base, hydroxylamine and water are blended to obtain the objective treating solution composition after ashing. A substrate is subjected to ashing after etching using a photoresist pattern disposed on the substrate as a mask and then the substrate is treated by applying the treating solution composition.

## LEGAL STATUS

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## CLAIMS

## [Claim(s)]

[Claim 1] (a) The salt of a hydrofluoric acid and the base which does not contain a metal ion, the (b) hydroxylamine, and the processing liquid constituent after ashing which comes to blend (c) water.

[Claim 2] (a) The processing liquid constituent after ashing according to claim 1 whose remainder the (b) component is blended for a component one to 45% of the weight 0.05 to 10% of the weight, and is the (c) component.

[Claim 3] (a) The processing liquid constituent after ashing according to claim 1 or 2 whose base which does not contain the metal ion for forming a component is at least one sort chosen from hydroxylamines, the 1st class, the 2nd class or the 3rd class fatty amine, an alicyclic amine, aromatic amine, heterocyclic amine, aqueous ammonia, and a low-grade alkyl quaternary-ammonium-salt radical.

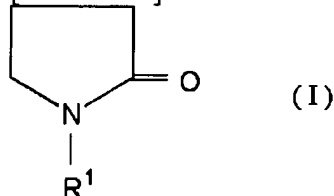
[Claim 4] (a) The processing liquid constituent after ashing given in any 1 term of claims 1-3 whose component is ammonium fluoride.

[Claim 5] The processing liquid constituent after ashing given in any 1 term of claims 1-4 which furthermore come to blend (d) aqueous ammonia.

[Claim 6] (a) The processing liquid constituent after ashing according to claim 5 whose remainder the 1 - (d) component is blended [ a component ] for the (b) component 0.05 to 5% of the weight 45% of the weight 0.05 to 10% of the weight, and is the (c) component.

[Claim 7] Furthermore, it is the (e) following general formula (I).

## [Formula 1]

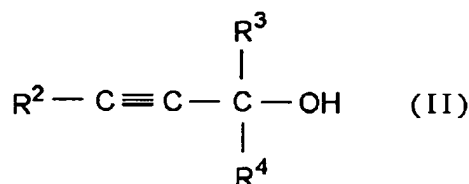


It is a processing liquid constituent after ashing given in any 1 term of claims 1, 3-5 which come to blend the N-alkyl-2-pyrrolidone expressed with (R<sup>1</sup> shows the alkyl group of the carbon atomic numbers 6-20 among a formula), and at least one sort of surfactants chosen from acetylene alcohol alkylene oxide addition products.

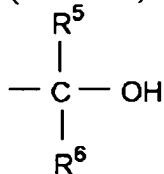
[Claim 8] (a) The processing liquid constituent after ashing according to claim 7 whose remainder the (b) component is blended [ a component ] for the 1 - (d) component 5% of the weight 45% of the weight 0.05 to 10% of the weight at a rate that the 0.05 - (e) component is 100-5000 ppm, and is the (c) component.

[Claim 9] (e) The acetylene alcohol for forming the acetylene alcohol alkylene oxide addition product of a component is the following general formula (II).

## [Formula 2]



(However, R2 a hydrogen atom or [Formula 3])



example; -- R3, R4, R5, and R6 -- respectively -- independent -- the alkyl group of a hydrogen atom and the carbon atomic numbers 1-6 -- being shown -- the processing liquid constituent after ashing according to claim 7 or 8 which is a compound expressed.

[Claim 10] (e) The processing liquid constituent after ashing given in any 1 term of claims 7-9 whose alkylene oxide for forming the acetylene alcohol alkylene oxide addition product of a component is ethylene oxide, propylene oxide, or such mixture.

[Claim 11] The processing liquid constituent after ashing given in any 1 term of claims 1-10 whose pH in a system is 8.5-13.5.

[Claim 12] (I) The process and (II) which prepare a photoresist layer on the substrate which has a metal layer The process which exposes this photoresist layer alternatively, (III) The process which develops the photoresist layer after exposure and prepares a photoresist pattern, (IV) The process which etches a substrate by using this photoresist pattern as a mask, and forms a metal circuit pattern, (V) The process and (VI) which carry out ashing of the photoresist pattern The process which the substrate after an ashing process is contacted to a processing liquid constituent, and processes it, and (VII) the process which carries out rinse processing of the substrate with water further after the above-mentioned processing -- since -- art characterized by processing a substrate using the processing liquid constituent of a publication in any 1 term of claims 1-11 in the art of the becoming substrate.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the art which used the processing liquid constituent after ashing, and this. It is related with the art using the processing liquid constituent and this which are excellent in dry etching and processing of a substrate in which ashing was performed continuously, in more detail by using as a mask the photoresist pattern prepared on the substrate. Especially this invention processing liquid constituent has high removal capacity also to the photoresist deterioration film metallurgy group deposition which produced the substrate with which 0.2-0.3 micrometers or the overly detailed photoresist pattern not more than it was formed after carrying out ashing, etching and, and is excellent in the corrosion prevention effectiveness of various metal wiring, a metal layer, and the metal insulating layer by which CVD vacuum evaporation was carried out. This invention is used suitable for manufacture of semiconductor devices, such as IC and LSI, or a liquid crystal panel component.

[0002]

[Description of the Prior Art] Semiconductor devices and liquid crystal panel components, such as IC and LSI, A photoresist is applied to homogeneity on insulating layers, such as the metal layer by which CVD vacuum evaporation was carried out on the substrate, and SiO two-layer. Carry out exposure and a development for this alternatively, and a photoresist pattern is formed. After etching alternatively the substrate with which semi-conductor layers, such as insulating layers by which CVD vacuum evaporation was carried out [ above-mentioned ] by using this pattern as a mask, such as a metal layer and SiO two-layer, and low-temperature polish recon film, amorphous silicon film, were formed and forming a detailed circuit, an unnecessary photoresist layer is removed and it is manufactured.

[0003] As the metal layer by which CVD vacuum evaporation was carried out [ above-mentioned ] here \*\*, aluminum (aluminum); Aluminum-silicon (aluminum-Si), Aluminium alloy (aluminum alloy); titanium (Ti), such as aluminum-copper (aluminum-Cu) and aluminum-silicon-copper (aluminum-Si-Cu); Titanium nitride (TiN), titanium-alloys [ , such as a titanium tungsten (TiW), ] (Ti alloy); -- various things, such as a tantalum (Ta), tantalum nitride (TaN), a tungsten (W), and a nitriding tungsten (WN), use -- having -- coming -- these -- monolayer - more than one are formed on a substrate in a layer.

[0004] By the way, in connection with the densification of an integrated circuit in recent years, the dry etching in which detailed etching of high density is more possible is in use. Moreover, plasma ashing is performed on the occasion of the unnecessary photoresist layer removal after etching. When the residues, such as photoresist deterioration film, serve as corniform, and it remains, or the residue object of the other component origin adheres to a flank, a pars basilaris ossis occipitalis, etc. of a pattern, and it remains by these etching and ashing processing and the metal layer at the time of etching is deleted, metal deposition will occur. Then, if these are not removed completely, problems, such as causing the yield fall of semi-conductor manufacture, will be produced.

[0005] The thing of the presentation from which these residue objects and deposition differed,

respectively according to the class and ashing conditions of etching gas, the class of metal with which it is formed on a substrate, the class of insulating layer, the class of photoresist to be used, etc. is generated. The present condition is that there are not a processing liquid constituent which it is difficult for a residue object and deposition to also become complicated and to trace these presentations etc., therefore calls this by various-ization of the severity of the processing conditions in various processings accompanying various amelioration of a semi-conductor in recent years, the metal used, an insulating layer, and a photoresist etc., and can be satisfied, and an art.

[0006] further -- recently -- that of a pattern -- much more -- the inclination of detailed-izing -- it is -- less than [ 0.2-0.3 micrometers or it ] -- the thing of a detailed pattern has overly come to be used. a demand of as opposed to [ in such a substrate with which the detailed pattern was overly formed, will become severe / one layer of condition nearby of etching and ashing / , and ] the anti-corrosiveness of metal wiring, the detachability of a residue object, etc. -- the former -- comparing -- markedly -- alike -- a high thing -- becoming -- \*\*\*\* -- the conventional processing liquid constituent -- current -- it is impossible overly to correspond to a detailed-ized process

[0007] As a former and photoresist deterioration film removal liquid constituent or the processing liquid constituent after ashing, Although the constituent containing fluorine system compounds, such as a hydrofluoric acid, is used abundantly As such an example, for example, specific quarternary ammonium salt and a specific fluorine compound, The semiconductor device cleaning agent which furthermore contains an organic solvent (JP,7-201794,A), The salt and the water-soluble organic solvent of a hydrofluoric acid and the base which does not contain a metal ion are included. pH of a system The exfoliation liquid constituent for resists of 5-8 (JP,9-197681,A), A fluorine compound, a water-soluble organic solvent, and the cleaning agent for semiconductor devices that carries out the amount content of specification of the water, respectively (JP,11-67632,A), The remover (JP,9-283507,A) which contains a specific quaternary ammonium hydroxide, the nucleophilicity amine compound which has an oxidation reduction potential, a saccharide and/or sugar-alcohol, and water by the specific blending ratio of coal, respectively is known.

[0008] However, in conventional exfoliation liquid given in each [ these ] official report, and a cleaning agent, it is becoming difficult for residue objects, such as photoresist deterioration film and metal deposition, to be removed certainly, preventing the corrosion of metal wiring under current 0.2-0.3 micrometers or current cruel etching not more than it overly in a detailed patternizing process, and an ashing processing condition.

[0009] Moreover, in the exfoliation liquid and the cleaning agent containing fluorine system compounds, such as a hydrofluoric acid, after processing of exfoliation, washing, etc., although indifferent-water rinse processing is performed, there is a problem that corrosion tends to take place at this time.

[0010]

[Problem(s) to be Solved by the Invention] This invention was made in view of the above-mentioned situation, and is set to 0.2-0.3 micrometers or the dry etching which is a severe condition rather than it can overly set in a detailed patternizing process following it curves, and the substrate with which ashing was performed continuously. While preventing the corrosion to metal wiring and being able to remove certainly residue objects, such as photoresist deterioration film and metal deposition It aims at offering the processing liquid constituent after ashing which can prevent effectively the corrosion in the time of residue object removal processing and a water rinse, and the art using this.

[0011]

[Means for Solving the Problem] this invention persons in the processing liquid constituent of the conventional hydrofluoric-acid content If the content of a hydrofluoric acid is reduction-ized, sufficient removal capacity of a residue object will not be acquired. Conversely, problems, like if the content of a hydrofluoric acid is increased, the corrosion to a metal layer or a metal oxidizing zone will take place occur. The result of having repeated examination wholeheartedly in view of the point that it is difficult to balance both in order to suppress the effect of this hydrofluoric acid as much as possible, It came to complete a header and this invention for the ability of the above-mentioned technical problem to be

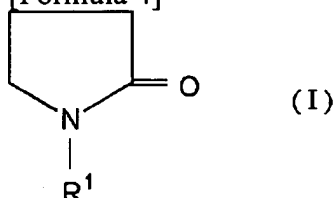
solved by combining and blending a specific component with the salt of a hydrofluoric acid and the base which does not contain a metal ion.

[0012] That is, this invention relates to the processing liquid constituent after the salt of the (a) hydrofluoric acid and the base which does not contain a metal ion, the (b) hydroxylamine, and ashing that comes to blend (c) water.

[0013] Moreover, it adds to the - (c) component (above-mentioned [ a ]), and this invention is (d) aqueous ammonia and/or the (e) following general formula (I) further.

[0014]

[Formula 4]



[0015] It is related with the processing liquid constituent after ashing which comes to blend the N-alkyl-2-pyrrolidone expressed with (R1 shows the alkyl group of the carbon atomic numbers 6-20 among a formula), and at least one sort of surfactants chosen from acetylene alcohol alkylene oxide addition products.

[0016] The above-mentioned processing liquid constituent has that desirable whose pH in a system is 8.5-13.5.

[0017] Moreover, this invention is (I). The process which prepares a photoresist layer on the substrate which has a metal layer, (II) Process which exposes this photoresist layer alternatively (III), the process which develops the photoresist layer after exposure and prepares a photoresist pattern, (IV) The process which etches a substrate by using this photoresist pattern as a mask, and forms a metal circuit pattern, (V) The process which carries out ashing of the photoresist pattern, and (VI) The process which the substrate after an ashing process is contacted to a processing liquid constituent, and processes it, and (VII) the process which carries out rinse processing of the substrate with water further after the above-mentioned processing -- since -- in the art of the becoming substrate, it is related with the art characterized by processing a substrate using the above-mentioned processing liquid constituent.

[0018]

[Embodiment of the Invention] Hereafter, this invention is explained in full detail.

[0019] The (a) component used for the processing liquid constituent of this invention is the salt of a hydrofluoric acid and the base which does not contain a metal ion. Here, as a base which does not contain a metal ion, organic amines, such as fatty amine of hydroxylamines, the 1st class, the 2nd class, or the 3rd class, an alicyclic amine, aromatic amine, and heterocyclic amine, aqueous ammonia, a low-grade alkyl quaternary-ammonium-salt radical, etc. are used preferably.

[0020] As hydroxylamines, hydroxylamine (NH<sub>2</sub>OH), N-methyl hydroxylamine, N, and N-dimethyl hydroxylamine, N, and N-diethylhydroxylamine etc. is specifically illustrated.

[0021] As the 1st class fatty amine, monoethanolamine, ethylenediamine, 2-(2-aminoethyl amino) ethanol, etc. are specifically illustrated.

[0022] As the 2nd class fatty amine, diethanolamine, a dipropyl amine, 2-ethylamino ethanol, etc. are specifically illustrated.

[0023] As the 3rd class fatty amine, dimethylamino ethanol, ethyl diethanolamine, etc. are specifically illustrated.

[0024] As an alicyclic amine, cyclohexylamine, dicyclohexylamine, etc. are specifically illustrated.

[0025] As aromatic amine, benzylamine, dibenzylamine, N-methylbenzyl amine, etc. are specifically illustrated.

[0026] As heterocyclic amine, a pyrrole, a pyrrolidine, a pyrrolidone, a pyridine, a morpholine, pyrazine, a piperidine, N-hydroxyethyl piperidine, oxazole, a thiazole, etc. are specifically illustrated.

[0027] As a low-grade alkyl quaternary-ammonium-salt radical, tetramethylammonium hydroxide (= TMAH), tetraethylammonium hydroxide, tetrapropylammonium hydroxide, trimethyl ethylammonium hydroxide, trimethylammonium (2-hydroxyethyl) hydroxide, triethyl (2-hydroxyethyl) ammonium hydroxide, TORIPURO (2-hydroxyethyl) pill ammonium hydroxide, trimethylammonium (1-hydroxypropyl) hydroxide, etc. are specifically illustrated.

[0028] Especially, aqueous ammonia, monoethanolamine, tetramethylammonium hydroxide, and trimethylammonium (2-hydroxyethyl) hydroxide are preferably used for the top where acquisition is easy from points, such as excelling in safety.

[0029] The base which does not contain a metal ion may use only one sort, or may use it combining two or more sorts.

[0030] The salt of the base and hydrofluoric acid which do not contain these metal ions can be manufactured by adding the base which does not contain a metal ion in the hydrofluoric acid of commercial 50 - 60% concentration of hydrogen fluoride so that pH may become five to about eight. As such a salt, ammonium fluoride (NH<sub>4</sub>F) is used most preferably. (a) A component can use one sort or two sorts or more.

[0031] (b) A hydroxylamine (NH<sub>2</sub>OH) is used as a component.

[0032] (c) Although the water of a component is inevitably contained in the (b) component etc., it is further blended by this invention.

[0033] By blending the (a) component, the (b) component, and the (c) component, in the substrate with which 0.2-0.3 micrometers or the overly detailed pattern not more than it was formed, this invention processing liquid constituent can prevent the corrosion to metal wiring, and can remove certainly residue objects, such as photoresist deterioration film and metal deposition. Moreover, the corrosion in the time of residue object removal processing and a water rinse can be prevented effectively.

[0034] From the point of balancing more effectively the detachability of a residue object, and the anti-corrosiveness of metal wiring in this invention processing liquid constituent, among this invention processing liquid constituent, the upper limit of the loadings of the (a) component has 10 desirable % of the weight, and is especially desirable. [ of 5 % of the weight ] Moreover, 0.05 % of the weight of a minimum is desirable, and its 0.1 % of the weight is especially desirable.

[0035] By the same reason as the above, the upper limit of the loadings of the (b) component has 45 desirable % of the weight, and 30 % of the weight is especially desirable. Moreover, 1 % of the weight of a minimum is desirable, and its 2 % of the weight is especially desirable.

[0036] (c) The loadings for outcrossing composition contain a component by the remainder during [ all ] a presentation.

[0037] In addition to the - (c) component (above-mentioned [ a ]), this invention processing liquid constituent can blend the (d) component and/or the (e) component further.

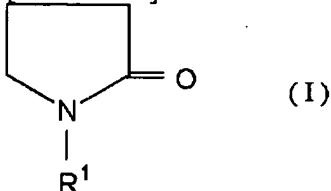
[0038] In this invention, aqueous ammonia is used as a (d) component. (d) By blending a component, the corrosion of metal wiring can be prevented more effectively.

[0039] Among this invention processing liquid constituent, the upper limit of the loadings of the (d) component has 5 desirable % of the weight, and is especially desirable. [ of 4 % of the weight ] Moreover, 0.05 % of the weight of a minimum is desirable, and its 0.1 % of the weight is especially desirable.

[0040] Moreover, at this invention, it is the following general formula (I) as a (e) component.

[0041]

[Formula 5]



[0042] The N-alkyl-2-pyrrolidone expressed with (R1 shows the alkyl group of the carbon atomic numbers 6-20 among a formula) and at least one sort of surfactants chosen from acetylene alcohol alkylene oxide addition products are used.

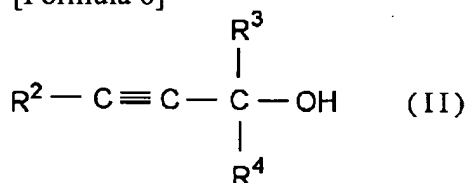
[0043] (e) A component is the well-known matter in itself as a surfactant. In this invention, in case the permeability of the processing liquid constituent itself can be raised, wettability can be raised and a hole pattern etc. is formed by blending this (e) component, a touch area with a pattern side face becomes large. It is thought that removal capacity, such as metal deposition generated at the pattern pars basilaris ossis occipitalis by it, improves.

[0044] As an example of the N-alkyl-2-pyrrolidone shown by the above-mentioned general formula (I) An N-hexyl-2-pyrrolidone, an N-heptyl-2-pyrrolidone, an N-octyl-2-pyrrolidone, An N-nonyl-2-pyrrolidone, an N-DESHIRU-2-pyrrolidone, an N-undecyl-2-pyrrolidone, An N-dodecyl-2-pyrrolidone, an N-tridecyl-2-pyrrolidone, An N-tetradecyl-2-pyrrolidone, an N-pentadecyl-2-pyrrolidone, an N-hexadecyl-2-pyrrolidone, an N-heptadecyl-2-pyrrolidone, an N-octadecyl-2-pyrrolidone, etc. are mentioned. Especially, the N-octyl-2-pyrrolidone and the N-dodecyl-2-pyrrolidone are marketed as "SURFADONE LP100" and "SURFADONE LP300" (all are made in eye ESUPI Japan above), respectively, and are used suitably.

[0045] As acetylene alcohol which forms this addition product in an acetylene alcohol alkylene oxide addition product, it is the following general formula (II).

[0046]

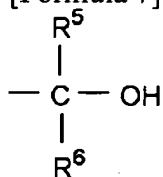
[Formula 6]



*Solve*

[0047] R2 [ however, ] -- a hydrogen atom -- or [0048]

[Formula 7]



[0049] example; -- R3, R4, R5, and R6 -- respectively -- independent -- the alkyl group of a hydrogen atom and the carbon atomic numbers 1-6 -- being shown -- the compound expressed is used preferably. As an alkyl group of the carbon atomic numbers 1-6, methyl group, ethyl group, propyl group, isopropyl group, butyl, isobutyl radical, sec-butyl, tert-butyl, pentyl radical, isopentyl radical, neopentyl radical, tert-pentyl radical, hexyl group, iso hexyl group, 3-methyl pentyl radical, 2, and 2-dimethyl butyl, 2, and 3-dimethyl butyl etc. is illustrated here.

[0050] This acetylene alcohol is marketed as series, such as "SAFI Norian" and "ORUFIN" (all are the products made from Air Product and Chemicals Inc. above), and is used suitably. "SAFI Norian 104", "SAFI Norians 82", or such mixture are most suitably used from the physical-properties side especially. "ORUFINB", "ORUFINP", "ORUFINY", etc. can be used for others.

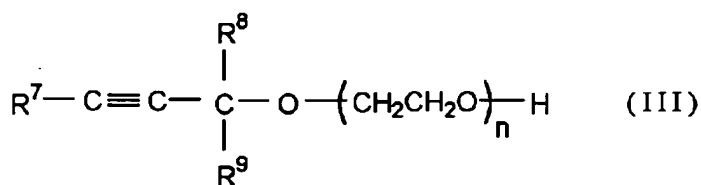
[0051] As alkylene oxide added to the above-mentioned acetylene alcohol, ethylene oxide, propylene oxide, or its mixture is used preferably.

[0052] At this invention, it is the following general formula (III).

[0053]

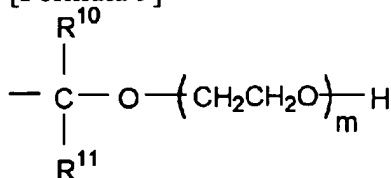
[Formula 8]





[0054] R7 [ however, ] -- a hydrogen atom -- or [0055]

[Formula 9]



[0056] example; -- R8, R9, R10, and R11 -- respectively -- independent -- the alkyl group of a hydrogen atom and the carbon atomic numbers 1-6 -- being shown -- the compound expressed is used preferably. (n+m) expresses the integer to 1-30, and changes properties, such as solubility to water, and surface tension, delicately with the number of addition of this ethylene oxide here.

[0057] The acetylene alcohol alkylene oxide addition product is marketed as the series of "SAFI Norian" (product made from Air Product and Chemicals Inc.), or series of "ASECHIRE Norian" (Kawaken Fine Chemicals Co., Ltd. make), and is used suitably. If change of properties, such as solubility to the water by the number of addition of ethylene oxide and surface tension, etc. is taken into consideration especially, "SAFI Norian 440" (n+m=3.5), "SAFI Norian 465" (n+m=10), "SAFI Norian 485" (n+m=30), "ASECHIRE Norian EL" (n+m=4), "ASECHIRE Norians EH" (n+m=10), or those mixture will be used suitably. The mixture of "ASECHIRE Norian EL" and "ASECHIRE Norian EH" is used especially preferably. What mixed "ASECHIRE Norian EL" and "ASECHIRE Norian EH" at a rate of 2:8-4:6 (weight ratio) is used especially suitably.

[0058] Among this invention processing liquid constituent, the upper limit of the loadings of the (e) component has desirable 5000 ppm, and is especially desirable. [ of 3000 ppm ] Moreover, 100 ppm of a minimum are desirable and its 300 ppm are especially desirable. (e) When a component increases more than the above-mentioned loadings range, it is difficult to be able to consider generating of air bubbles, to be unable to desire improvement in the further effectiveness, even if wettability improvement is saturated and it adds it more than it, but to, acquire wettability sufficient effectiveness to search for on the other hand, when fewer than the above-mentioned range. In addition, suitable loadings differ somewhat by the case where the case where an N-alkyl-2-pyrrolidone is used as a (e) component, and an acetylene alcohol alkylene oxide addition product are used, and the loadings around 500 ppm are desirable in an N-alkyl-2-pyrrolidone at about 1000-2000 ppm and an acetylene alcohol alkylene oxide addition product. (e) A component can use one sort or two sorts or more.

[0059] Anticorrosives can be further blended with this invention processing liquid constituent if needed. As being chosen from the group which becomes an aromatic series hydroxy compound, acetylene alcohol, a carboxyl group content organic compound and its anhydride, a triazole compound, and a list from a saccharide especially, although anticorrosives can use the anticorrosives used for conventional organic amine system exfoliation liquid for arbitration, one sort is preferably used as it is few. }

[0060] The processing liquid constituent after ashing of this invention can be used in an alkali water solution in favor of the photoresist in which development is possible including a negative mold and a positive type photoresist. The positive type photoresist which contains the (i) naphthoquinonediazide compound and novolak resin as such a photoresist, (ii) The positive type photoresist containing the compound which generates an acid by exposure, the compound with which it decomposes an acid and the solubility over an alkali water solution increases, and alkali fusibility resin, The compound which generates an acid by exposure, the positive type photoresist containing the alkali fusibility resin which has the radical on which an acid decomposes into and the solubility over an alkali water solution

increases, (iii) And although the negative-mold photoresist containing the compound, the cross linking agent, and alkali fusibility resin which generate an acid by (iv) light etc. is mentioned, it is not limited to these.

[0061] The art of this invention is (I). The process which prepares a photoresist layer on the substrate which has a metal layer, (II) Process which exposes this photoresist layer alternatively (III), the process which develops the photoresist layer after exposure and prepares a photoresist pattern, (IV) The process which etches a substrate by using this photoresist pattern as a mask, and forms a metal circuit pattern, (V) The process which carries out ashing of the photoresist pattern, and (VI) The process which the substrate after an ashing process is contacted to a processing liquid constituent, and processes it, and (VII) the process which carries out rinse processing of the substrate with water further after the above-mentioned processing -- since -- it consists of processing a substrate using the above-mentioned this invention processing liquid constituent in the art of the becoming substrate.

[0062] On substrates, such as a silicon wafer and glass, by vacuum evaporation etc., an organic SOG layer etc. is prepared by request at a metal and a metal oxidizing zone, and a pan for semi-conductor layers, such as insulating layers, such as SiO<sub>2</sub> film, low-temperature polish recon film, and amorphous silicon film, and flattening, and specifically, a photoresist layer is continuously formed on these layers.

[0063] As the above-mentioned metal and metal oxidizing zone, (Aluminum aluminum); aluminum-silicon (aluminum-Si), Aluminium alloy (aluminum alloy); titanium (Ti), such as aluminum-copper (aluminum-Cu) and aluminum-silicon-copper (aluminum-Si-Cu); Titanium nitride TiN, Titanium alloys, such as a titanium tungsten (TiW) (Ti alloy); a tantalum (Ta), tantalum nitride (TaN), a tungsten (W), a nitriding tungsten (WN), etc. are used, and these are formed on a substrate in monolayer - two or more layers. Since a residue object adheres and it is easy to produce deposition when ashing processing of a back process is performed if it is in Ti alloys, such as aluminum alloy; Ti; TiN, such as aluminum; aluminum-Si, aluminum-Cu, and aluminum-Si-Cu, and TiW, especially, the processing liquid constituent of this invention can demonstrate the effectiveness exceptionally to the corrosion prevention of these metals and a metal oxidizing zone at the removal list of the residue object.

[0064] An organic SOG layer can use a well-known thing. An SOG layer is the silicon oxide film which silicon compound content coating liquid is applied on a substrate, and is formed, and an organic SOG layer has the configuration which the organic radical of low-grade alkali (for example, CH<sub>3</sub> grade) combined with Si of this silicon oxide film.

[0065] Subsequently, a photoresist pattern is formed. Exposure and development conditions can be suitably chosen by the photoresist used according to the purpose. Exposure irradiates a photoresist layer, exposing a photoresist layer through a desired mask pattern, or scanning an electron ray with the light source which emits light in activity beams of light, such as ultraviolet rays, far ultraviolet rays, excimer laser, an X-ray, and an electron ray, for example, a low pressure mercury lamp, a high pressure mercury vapor lamp, an ultrahigh pressure mercury lamp, a xenon lamp, etc. Then, exposure afterbaking processing (postexposure BEKU) is performed if needed.

[0066] Next, pattern development can be performed using the developer for photoresists, and a predetermined photoresist pattern can be obtained. In addition, after carrying out fixed time amount immersion of the substrate with which especially the development approach is not limited and the photoresist was applied at a developer, Various development according to the purpose, such as spray development which carries out rinsing desiccation after carrying out the spray of the developer to the paddle development and the photoresist front face which rinse, trickle a developer into the front face of the photoresist to dry, and which was immersion-developed and was applied, and carry out rinsing desiccation after carrying out fixed time amount gentle placement, can be carried out.

[0067] Subsequently, after etching the above-mentioned metal layer and an insulating layer by dry etching etc. alternatively by using the formed photoresist pattern as a mask and forming a detailed circuit, plasma ashing removes an unnecessary photoresist layer. At this time, the metal deposition generated at the time of the resist residue after ashing (photoresist deterioration film) or metal layer etching adheres and remains as a residue object on a substrate front face.

[0068] These residue object is contacted to this invention processing liquid constituent, and the residue

object metallurgy group deposition on a substrate is removed. By using this invention processing liquid constituent, residue objects, such as these photoresist deterioration film metallurgy group deposition, are removed easily. It excels in the corrosion prevention effectiveness over the substrate which has metals, such as aluminum and aluminum alloy, especially.

[0069] In addition, contact to the processing liquid constituent of the substrate after ashing is performed by approaches, such as a paddle method, a dip method, and the shower method. Here, a paddle method is an art of single wafer processing, and after dropping a penetrant remover from a nozzle for every substrate and contacting fixed time amount processing liquid and a substrate using surface tension, it means the approach of processing by rotating a substrate with a spinner etc. and flying liquid. A dip method means the approach of processing by carrying out fixed time amount immersion of the wafer the whole wafer cassette into the tub filled with the processing liquid constituent. The shower method rotates a wafer the whole cassette and means the approach of processing by spraying processing liquid from two or more nozzles from the one direction.

[0070] Water rinse processing is performed after the above-mentioned residue object removal processing. By this invention, corrosion can be prevented to having been easy to generate corrosion conventionally at the time of this water rinse processing in the exfoliation liquid containing fluorine system compounds, such as a hydrofluoric acid, or a cleaning agent at the time of water rinse processing.

[0071] The processing liquid constituent of this invention and the art using this have the removal nature which was excellent to the photoresist deterioration film metallurgy group deposition which produced the substrate with which 0.2-0.3 micrometers or the overly detailed photoresist pattern not more than it was formed after carrying out ashing, etching and, and can prevent effectively the corrosion to various metal wiring, a metal layer, etc.

[0072]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, unless it mentions specially, weight % shows loadings.

[0073] (Examples 1-5, examples 1-5 of a comparison)

[0074] Let the silicon wafer in which it formed [removal nature of residue object after ashing] SiO<sub>2</sub> two-layer be a substrate, On this substrate, spinner spreading of THMR-iP3300 (TOKYO OHKA KOGYO CO., LTD. make) which is the positive type photoresist constituent which forms an aluminum-Cu layer as the 2nd layer, forms a TiN layer as the 3rd layer, and consists a TiN layer of a naphthoquinonediazide compound and novolak resin on this as the 1st layer was carried out, prebaking for 90 seconds was given at 90 degrees C, and the photoresist layer of 0.2 micrometers of thickness was formed. This photoresist layer was exposed through the mask pattern using NSR-2005i10D (NIKON CORP. make), the development was carried out using the tetramethylammonium hydroxide (TMAH) water solution 2.38% of the weight, and the photoresist pattern of 0.3-micrometer Rhine - and - tooth space was obtained. Subsequently, postbake for 90 seconds was performed at 120 degrees C.

[0075] Next, etching processing of the substrate was carried out for 168 seconds at pressure 5mmTorr and the stage temperature of 20 degrees C by having made the mixed gas of chlorine and boron trichloride into etchant using etching system TSS-6000 (TOKYO OHKA KOGYO CO., LTD. make) to the above-mentioned substrate, and, subsequently after corrosion processing (processing except a chlorine atom) was performed for 30 seconds at pressure 20mmTorr and the stage temperature of 20 degrees C using oxygen and the mixed gas of trifluoromethane.

[0076] Next, pressure 1.2mmTorr was performed by ashing device TCA-3822 (TOKYO OHKA KOGYO CO., LTD. make), and plasma ashing processing of a photoresist pattern was performed for 40 seconds at the stage temperature of 220 degrees C.

[0077] Then, you made it immersed for 10 minutes, and 23 degrees C of removal processings of the residue object after ashing were performed to the processing liquid constituent which shows the above-mentioned substrate processed [ plasma ashing ] in Tables 1-2. Rinse processing of the substrate which processed was carried out with pure water, the removal condition of a residue object was observed with the SEM (scanning electron microscope) photograph, and the following criteria estimated. A result is

shown in Tables 1-2.

(Evaluation)

O : x from which the residue object was removed completely: The residue object remained considerably. [0078] aluminum wiring was prepared on the silicon wafer in which it formed [anti-corrosiveness [ to metal wiring ] (aluminum dirty rate)] SiO two-layer. The 23 degrees C of the amounts of film decreases of aluminum wiring after carrying out immersion processing for 20 minutes were measured using "DekTak 3030 Auto 2" (product made from ULVAC) which is a level difference measuring device to 20% water-solution processing liquid constituent which diluted with water each processing liquid constituent which shows this in Tables 1-2 5 times, respectively. The amount of film decreases around for 1 minute after a measurement value was calculated, and the dirty rate (angstrom/min) of aluminum was computed. A result is shown in Tables 1-2.

[0079]

[Table 1]

組 成 (重量%)		実 施 例				
		1	2	3	4	5
(a)成分	フッ化アンモニウム (NH <sub>4</sub> F)	0.5	0.5	0.5	0.5	0.5
(b)成分	ヒドロキシルアミン (NH <sub>2</sub> OH)	15	15	5	15	15
(c)成分	水	残 部	残 部	残 部	残 部	残 部
(d)成分	アンモニア水	0.5	—	0.5	0.5	0.5
(e)成分	N-オクチル-2-ピロリドン	—	—	—	500ppm	—
	アセチレンアルコール・アルキレンオキシド付加物	—	—	—	—	1000 ppm
pH		9.6	8.7	9.5	9.6	9.6
残渣物の除去性		○	○	○	○	○
A1 エッチレート (Å/ストローク/min)		5.6	6.3	6.1	5.4	5.5

[0080]

[Table 2]

組 成 (重量%)		比 較 例				
		1	2	3	4	5
(a)成分	フッ化アンモニウム (NH <sub>4</sub> F)	1	1	1	1	—
(b)成分	ヒドロキシルアミン (NH <sub>2</sub> OH)	—	—	—	—	15
(c)成分	水	30	30	30	50	65
(d)成分	アンモニア水	—	—	—	—	—
(e)成分	N-ドデシル-2-ピロリドン	—	—	—	—	—
	アセチレンアルコール・アルキレンオキシド付加物	1000 ppm	1000 ppm	—	—	—
その他 の成分	DMSO	残 部	残 部	残 部	—	—
	HF	—	0.05	—	—	—
	DMF	—	—	—	残 部	—
	TMAHのギ酸塩	—	—	—	10	—
	TMAH	—	—	—	—	10
	ソルビトール	—	—	—	—	10
pH		8.0	8.0	8.0	6.6	14.0 超
残渣物の除去性		○	○	○	○	×
A1エッチレート (オングストローム/min)		45.3	62.5	47.7	48.3	80.0 超

[0081] In addition, the mixture which mixed "ASECHIRE Norian EL" and "ASECHIRE Norian EH" at a rate of 3:7 (weight ratio) was used for the acetylene alcohol alkylene oxide addition product among Table 1-2.

[0082] moreover, the inside of Table 2 and DMSO -- dimethyl sulfoxide -- DMF expresses N,N-dimethylformamide and, as for TMAH, HF expresses trimethylammonium hydroxide for a hydrofluoric acid, respectively.

[0083]

[Effect of the Invention] As explained in full detail above, while excelling in the dry etching of a severe condition, and the processability of the substrate with which ashing was performed more according to this invention, the processing liquid constituent after ashing which is excellent in the corrosion prevention effectiveness over the substrate with which the metal layer was formed, and the art using this are offered. The processing liquid constituent and art of this invention have high removal capacity to the photoresist deterioration film metallurgy group deposition which produced the substrate with which 0.2-0.3 micrometers or the overly detailed photoresist pattern not more than it was formed after carrying out ashing, etching and, and are excellent in the corrosion prevention effectiveness of various metal wiring (metal layer) and the metal insulating layer by which CVD vacuum evaporation was carried out. This invention can prevent effectively the corrosion in the time of residue object removal processing and a water rinse again.

[Translation done.]